# Radiolysis of Liquid Propane: non-Radical Reactions[1]

By. R. D. Koob [2] and Larry Kevan

Dept. of Chemistry, University of Kansas, Lawrence, Kansas 66044

The yields of ionic and excited molecule reactions in γ-radiolysis of liquid propane from 35 to −130°C have been assessed by isotopic analysis of $C_3H_8+C_3D_8+O_2$ and $CH_3CD_2CH_3+O_2$ mixtures. From a comparison with gas phase data the following conclusions are reached for the gas to liquid phase change: (*a*) the ionic decomposition yield decreases by ≤69 %, (*b*) the net excited molecule decomposition yield decreases by 7 % or less, (*c*) parent ion fragmentation still occurs in the liquid and exhibits fragmentation processes requiring from 1-4 eV excitation, (*d*) the $H_2^-/H^-$ transfer reaction ratio for $C_2H_4^+ + C_3H_8$ seems to be increased, and (*e*) the isotopic decomposition of $CH_3CD_2CH_3$ is drastically changed.

The gas phase reactions in γ-irradiated propane have been well characterized by Ausloos and co-workers [3-6] and Futrell and co-workers.[7-10] The fragmentation of both excited parent ions and neutral molecules are important in product formation. Evidence derived from mass spectral data [3-14] vacuum u.-v. photolysis,[4-6, 15] radiolysis in an electric field,[5] and radiolysis of isotopically labelled propane [3-10] has allowed quantitative assessment of fragmentation and subsequent reactions in propane radiolysis.

The availability of such extensive data and interpretation in the gas phase makes propane an ideal molecule to study for comparison between gas and liquid. Rare gas sensitization [16, 17] and thermal radical reactions [18] in radiolysis of liquid propane are discussed in other work. This paper treats non-radical reactions. Fragmentation of both parent ions and excited molecules is necessary to explain fully the observed liquid phase products.

## EXPERIMENTAL

Phillips research grade propane was purified by gas chromatography; the last remaining impurity, propene, was present in concentrations of less than 3 p.p.m. Deuterated propanes were about 95 % isotopically pure. Materials used as scavengers were purchased as high purity grades and were used without further purification. Samples were condensed into 4 cm long Pyrex ampoules fabricated from 2 mm int. diam. heavy-wall capillary tubing, and were irradiated by $Co^{60}$ gamma rays at a nominal dose rate of 0·5 Mrad/h to $H_2O$. In all samples the liquid phase occupied 80 % or more of the ampoule volume. In addition to irradiation at the gamma source temperature (35°C), samples were irradiated in solid $CO_2$ (−78°C) and in a liquid-nitrogen-cooled air stream (−130°C).

Ferrous sulphate dosimetry was used to determine the total dose to the sample. The dosimetry solution was $O_2$ saturated and irradiated in ampoules similar to those used with actual samples. The dosimetry results show that the actual dose to the liquid in the heavy-wall glass ampoules is about 5 % higher than if the liquid is irradiated in a vessel whose diameter is large compared to the average range of the secondary electrons produced by gamma radiation. The total dose absorbed by liquid propane was calculated by correcting the dose to the dosimetry solution using electron fraction (electron density) and stopping-power per electron [19] correction factors.

After irradiation, samples were analyzed by gas chromatography. All components of the sample, except isobutane, were determined in a single aliquot using a series-parallel arrangement of columns.[18, 20] $H_2$ was not determined.

Isotopic ratios were measured on a Nuclide model 12-90G mass spectrometer. Ethane and ethylene were trapped after gas chromatographic separation at 77°K from a helium stream; the helium was pumped away from the sample before it was injected into the mass spectrometer. Methane could not be trapped quantitatively from a helium stream so $CO_2$ was used as a carrier gas and methane was trapped at 77°K by total collection of the $CO_2$ stream. The sample was held at 77°K for mass spectrometric analysis so that only methane was injected.

Fragmentation patterns for $CD_4$, $CD_3H$, $CD_2H_2$, $CDH_3$, $CH_4$, $C_2D_6$, $C_2H_6$, $C_2D_4$ and $C_2H_4$ were measured for authentic samples on the Nuclide mass spectrometer. Other fragmentation patterns were obtained from the literature [21,22] and normalized to fragmentation patterns of knowns.

## RESULTS

Fig. 1 shows the yield in $G$ units, where $G$ equals the number of molecules produced per 100 eV of radiation energy absorbed, against phase and temperature for fragmentation products from propane irradiated to 1·2 Mrad in the presence of >1 % $O_2$. This dose corresponds to less than 0·10 % conversion in both phases. The product yield against dose up to 12 Mrad for $O_2$-scavenged propane showed no variation outside of experimental error. Therefore, the values are considered to be initial yields and to be directly related to the initial distribution of ions and molecules produced by radiation. The error in these numbers, as estimated from experimental scatter, is less than 15 %.

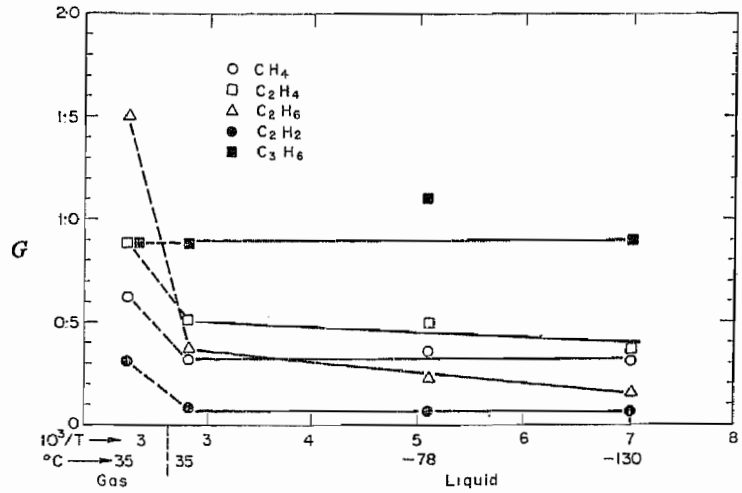


FIG. 1.—Radiolysis product yields $G$ in irradiated $C_3H_8+O_2$ against phase and temperature.

The phase change results in a decrease in $G$-value for propane loss in the $O_2$-scavenged system of 44 % [$G(-C_3H_8)$ = 2·88 in gas; $G(-C_3H_8)$ = 1·63 in liquid]. This decrease occurs entirely in the smaller fragmentation products (less than $C_3$). The propylene yield remains constant with the phase change. All yields, with the exception of that of ethane, remain constant or decrease only slightly as the liquid temperature is lowered. The ethane yield drops smoothly and at −130°C it has reached less than 50 % of its 35°C value.

Table 1 gives values for important isotopic fractions from analysis of the system, $C_3H_8+C_3D_8+O_2$. All ratios are normalized to represent a 1 : 1 ratio of $C_3H_8$ : $C_3D_8$. Isotopically-mixed propanes in $C_3D_8$ account for less than 5 % of the total

propane and corrections for these were minor or unnecessary. For a given compound the expression, (sum of isotopically pure components—sum of isotopically mixed components) /(sum of all components), is a direct measure of the fraction of the fraction of that compound formed intramolecularly. The isotopically mixed components arise from bimolecular reactions. If isotope effects are neglected, the yields of intramolecular and bimolecular reactions can be expressed in terms of only the more highly deuterated symmetrical components (e.g., $C_2D_6$ rather than $C_2D_6+C_2H_6$, $C_2D_5H$ rather than $C_2D_5H+C_2H_5D$, etc.). This is advantageous because the deuterated components are more accurately measured by mass spectrometry. Within experimental error, $C_2D_3H = C_2H_3D$, and $C_2D_5H = C_2H_5D$. In addition to the isotopic data in table 1 intramolecular $CH_4$ from $Ar+C_3H_8+C_3D_8+O_2$ (25 : 1 : 1 : 0·05) and $Xe+C_3H_8+C_3D_8+O_2$ (25 : 1 : 1 : 0·05) liquid mixtures was 80 %. Little change is seen in the amount of intramolecular against bimolecular modes of reaction in the change from gas to liquid or with decreasing temperature for the fractions investigated.

TABLE 1.—ISOTOPIC FRACTIONS IN IRRADIATED MIXTURES OF $C_3H_8+C_3D_8$-SCAVENGER[a]

| fraction | gas, 25°C | | | liquid | | |
|---|---|---|---|---|---|---|
| | 51-478 mm[b] scavenger→$I_2$, NO | 300 mm[c] NO | 760 mm[d] $C_4H_6$ | 35°C $O_2$ | −78°C $O_2$ | −130°C $O_2$ |
| $\frac{CD_4-CD_3H}{CD_4+CD_3H}$ | 0·72 | 0·85 | — | — | — | — |
| $\frac{C_2D_6-(C_2D_5H+C_2D_4H_2)}{C_2D_6+(C_2D_5H+C_2D_4H_2)}$ | 0·02 | 0·09 | 0·0 | 0·0 | 0·0 | 0·0 |
| $\frac{C_2D_4H_2}{C_2D_4H_2+C_2D_5H}$ | 0·11 | 0·10 | 0·12 | 0·26 | 0·40 | 0·43 |
| $\frac{C_2D_4-C_2D_3H}{C_2D_4-C_2D_3H}$ | 0·67 | 0·70 | 0·71 | 0·74 | 0·77 | 0·76 |

[a] all fractions have been corrected to $C_3D_8/C_3H_8 = 1$ ; [b] ref. (3) ; [c] ref. (5) ; [d] ref. (10).

Table 2 contains the isotopic analysis of methanes produced in the irradiation of the system $CH_3CD_2CH_3+O_2$. A marked increase in the amount of $CH_4$ relative to $CH_3D$ is seen when the phase is changed from gas to liquid. Comparison of the liquid data with data listed for high-pressure propane experiments in table 2 shows that the trend of $CH_3D/CH_4$ with increasing pressure does not extrapolate to the liquid.

TABLE 2.—ISOTOPIC ANALYSIS OF METHANE PRODUCED BY IRRADIATION OF $CH_3CD_2CH_3+O_2$ OR $CH_3CD_2CH_3+NO$

| | gas[a] | | liquid | | |
|---|---|---|---|---|---|
| | 500 mm NO | 8·65 atm NO | 35°C $O_2$ | −78°C $O_2$ | −130°C $O_2$ |
| $CH_4$ | 53·4 | 48·9 | 75 | 76 | 75 |
| $CH_3D$ | 41·3 | 46·7 | 18 | 17 | 18 |
| $CH_2D_2$ | 5·3 | 4·4 | 7 | 7 | 7 |
| $\frac{CH_3D}{CH_4}$ | 0·77 | 0·96 | 0·24 | 0·22 | 0·24 |

[a] ref. (3).

## DISCUSSION

We deal here with the formation of non-radical products, ethane, ethylene propylene and methane, in an $O_2$-scavenged system. The efficiency of $O_2$ as thermal radical scavenger in our system is substantiated by noting that typical radica

recombination products (butanes, pentanes and hexanes) are reduced below the limit of detection when $>1$ % $O_2$ is added. In the scavenged system we consider all products to arise by intramolecular decomposition of the parent ion and excited molecule or by bimolecular ionic reactions. Other bimolecular reactions, such as those involving excited free radicals, play only a minor role in the liquid. Intramolecular and bimolecular contributions to product formation are assessed by using $C_3H_8+C_3D_8+O_2$ mixtures as has been done in the gas phase.[3-10]

## ETHANE FORMATION

The entire ethane yield is accounted for by the bimolecular ionic reactions (1) and (2).

$$C_2H_5^+ + C_3H_8 \rightarrow C_2H_6 + C_3H_7^+ \quad (1)$$

$$C_2H_4^+ + C_3H_8 \rightarrow C_2H_6 + C_3H_6^+. \quad (2)$$

This is shown by the second line of data in table 1; $C_2D_5H$ is characteristic of reaction (1) and $C_2D_4H_2$ is characteristic of reaction (2). The isotopic data show that $C_2H_5^+$ and $C_2H_4^+$ ions are definitely produced in the radiolysis of liquid propane. The yield of $C_2D_3H_3$ is less than 2 % of the total ethane.

Reaction (3)

$$C_3H_8^* \rightarrow C_2H_6 + CH_2 \quad (3)$$

which is observed to form about 5 % of the total ethane in the gas [5, 10] is not observable ($<2$ % of total ethane) from our liquid phase data. The relative importance of reaction (2) to ethane production is given by the isotopic ratio in line 3 of table 1. The $H_2^-$ transfer reaction seems to be at least twice as important in the liquid phase as in the gas phase.

Table 3 summarizes the yields of various decomposition modes of excited ions and molecules in irradiated propane. The yield of $C_3H_8^+ {}^* \rightarrow C_2H_5^+ + CH_3$ is given by $[C_2D_5H/(C_2D_5H+C_2D_4H_2)]\ G(C_2H_6)$; all yields refer to the scavenged system.

TABLE 3.—DECOMPOSITION YIELDS $G$ OF EXCITED IONS AND NEUTRAL MOLECULES IN IRRADIATED PROPANE

| reaction | gas, 35°C, 1 atm | | liquid | | |
|---|---|---|---|---|---|
| | *a* | *b* | 35°C | −78°C | −130°C |
| $C_3H_8^+ {}^* \rightarrow C_2H_4^+ + CH_4$ | 0·61 | 0·34 | 0·15 | 0·19 | 0·16 |
| $\rightarrow C_2H_5^+ + CH_3$ | 1·3 | 1·3 | 0·27 | 0·14 | 0·09 |
| $\rightarrow C_3H_5^+ + H_2 + H$ | 0·25 | 0·28 | 0·13 | — | — |
| $\rightarrow C_2H_3^+ + CH_3 + H_2$ | 0·27 | 0·27 | 0·13 | 0·12 | 0·08 |
| $C_3H_8^* \rightarrow C_3H_6 + H_2$ | 0·54 | 0·60 | 0·75 | — | — |
| $\rightarrow C_2H_4 + CH_4$ | 0·17 | 0·16 | 0·10 | 0·10 | 0·07 |
| $\rightarrow C_2H_4 + CH_3 + H$ | 0·43 | 0·45 | 0·28 | 0·26 | 0·18 |

[a] averaged isotopic data from ref. (3), (5) and (10) (table 1); $G$ values calculated from M/N yields in ref. (10).

[b] averaged isotopic data from ref. (3), (5) and (10) (table 1); $G$ values from this work.

## ETHYLENE FORMATION

The isotopic ratio in line 4 of table 1 shows that 25 % of the ethylene arises from bimolecular ionic reactions; this is similar to the ratio observed in the gas phase. The equality of $C_2D_3H$ and $C_2H_3D$ yields allows us to assign 25 % of the ethylene to bimolecular reaction (4),

$$C_2H_3^+ + C_3H_8 \rightarrow C_2H_4 + C_3H_7^+. \quad (4)$$

The ionic decomposition yield to give $C_2H_3^+$ is given by $[2C_2D_3H/(C_2D_3H+C_2D_4)]$ $G(C_2H_4)_{bimolec}$ and is tabulated in table 3.

Isotopic data show that the remaining 75 % of the ethylene yield is produced by intramolecular decomposition. Since ethylene elimination from the propane ion is not a major decomposition mode for gas phase propane,[11] the intramolecular ethylene yield is assigned to neutral excited propane decomposition via reactions (5) and (6),

$$C_3H_8^* \rightarrow C_2H_4+CH_4 \quad (5)$$

$$C_3H_8^* \rightarrow C_2H_4+CH_3+H. \quad (6)$$

The relative yields of (5) and (6) have been assessed in the gas phase from radiolysis in an electric field; $k_5/k_6$ equals 0·36 based on methane and ethylene yields or 0·48 as a lower limit based on the $C_2D_3H/C_2D_2H_2$ ratio from $CD_3CH_2CD_3$.[5] These values depend on the assumption that excitation of propane induced by electrons accelerated in the electric field is similar to excitation of propane in radiolysis. The ratio $k_5/k_6$ can be evaluated independently from vacuum u.-v. photolysis of scavenged propane. We have re-investigated this by photolyzing $C_3H_8+O_2$ mixtures with Xe (8·4 eV) and Kr (10·0 eV) resonance lamps. The yield ratio of methane/(ethylene-methane) gives $k_5/k_6$ and equals $0{\cdot}51\pm0{\cdot}05$.[23] This value is in fair agreement with the electric field measurements [5] and indicates that the energy dependence of $k_5/k_6$ is not too strong. Since the average energy of excited neutral propane is probably less in the liquid than in the gas, the gas phase value of $k_5/k_6$ may be regarded as a lower limit in the liquid. We have therefore used $k_5/k_6 = 0{\cdot}36$ [5] to assess the contributions of reactions (5) and (6) in table 3; the yield of reaction (5) = $[k_5/k_5+k_6]G(C_2H_4)_{intramolec}$ and is regarded as a lower limit while the yield of reaction (6) = $[k_6/k_5+k_6]G(C_2H_4)_{intramolec}$ and is regarded as an upper limit.

## PROPYLENE FORMATION

The isotopic distribution of propylene was not measured because of experimental complications. In the gas phase, isotopic data [5, 7, 10] show that 68 % of the propylene comes from molecular decomposition and the remaining 32 % from hydride transfer involving $C_3H_5^+$. The analogous molecular decomposition and hydride transfer reactions that form ethylene occur in similar proportion in both gas and liquid phases. However, the total ethylene yield drops 42 % from gas to liquid while the total propylene yield remains constant. In the absence of liquid phase isotopic data, we assume that the $C_3H_5^+$ yield is not greater than the $C_2H_3^+$ yield in the liquid; contributions are shown in table 3.

$C_3H_7^+$ ions are formed in all hydride transfer reactions. In the liquid phase most of these ions will be neutralized to form $C_3H_7$ which will be scavenged. Some $C_3H_6$ may also be formed; this source of $C_3H_6$ is included in the $C_3H_6$ attributable to molecular decomposition.

## METHANE FORMATION

Isotopic analysis of the methane product fraction was not done for $C_3H_8$ $C_3D_8+O_2$ liquid mixtures but was done for $C_3H_8+C_3D_8+O_2$ mixtures in liquid argon and xenon. In all of these mixtures about 80 % of the methane is eliminated intramolecularly. The remaining 20 % is isotopically mixed which indicates formation by bimolecular reactions. A similar ratio is observed in the gas phase.[3, 5] Bimolecular processes that may give rise to isotopically mixed methane include

" hot " methyl radicals which are not scavenged and possibly hydride transfer to $CH_3^+$. In the following calculations, 20 % of the methane yield is attributed to bimolecular reactions.

Intramolecular elimination of methane may occur from neutral decomposition (5) or ionic decomposition (7),

$$C_3H_8^{+*} \rightarrow C_2H_4^+ + CH_4. \qquad (7)$$

The yield of reaction (5) has been calculated in table 3. The yield of reaction (7) is then calculated by difference from the observed intramolecular $CH_4$ yield $[0{\cdot}8G(CH_4)_{obs} - G(5) = G(7)]$; these values are tabulated in table 3. $G(7)$ is an upper limit since $G(5)$ is a lower limit and since a small contribution from $C_3H_8^{+*} \rightarrow C_2H_4^+ + CH_3 + H$ may be present.

In the gas phase an independent evaluation of the yields of reactions (5) and (7) is possible by measuring the isotopic methane eliminated from $CH_3CD_2CH_3$ or $CD_3CH_2CD_3$.[3-5] For $CH_3CD_2CH_3$ the excited neutral molecule fragments to give more $CH_3D$ than $CH_4$; 75 % and 85 % $CH_3D$ is obtained for excitation by Xe and Kr resonance lines, respectively. In contrast, the parent ion of $CH_3CD_2CH_3$ fragments to give mainly $CH_4$; 84 % and 75 % $CH_4$ is obtained for ionization by 13 and 70 eV electrons, respectively. Isotopic methane analysis [3-5] from propane radiolysis at 1 atm indicates that 64 % of the methane formed intramolecularly arises from an ionic mechanism (reaction (7)) and 36 % from a molecular mechanism (reaction (5)). This compares with values of 76 % from ionic mechanisms and 24 % from neutral mechanisms of intramolecular decomposition calculated by balancing yields.[10]

Isotopic methane data from $CH_3CD_2CH_3$ decomposition in the liquid phase is shown in table 2. The $CH_3D/CH_4$ ratio decreases by a factor of 2 in the liquid compared to that in the 1 atm gas; based on the analysis used in the gas phase, this ratio implies that the intramolecular methane is over 90 % ionic. This result conflicts with the average value of 65 % ionic in table 3 calculated by balancing yields. In the absence of liquid phase photolysis data on $CH_3CD_2CH_3$ we conclude that the isotopic intramolecular methane from $CH_3CD_2CH_3$ is *not* a valid measure of the relative importance of reactions (5) and (7) in the liquid phase. This may be related to the fact that both reactions (5) and (7) shift toward $CH_4$ elimination at lower energies.

The yield of molecular methane from ionic elimination calculated in table 3 equals the $C_2H_4^+$ yield. $C_2H_4^+$ undergoes the $H_2^-$ and $H^-$ transfer reactions (2) and (8):

$$C_2H_4^+ + C_3H_8 \rightarrow C_2H_5 + C_3H_7^+. \qquad (8)$$

The rate ratio, $k_2/(k_2+k_8)$, has been measured by high pressure mass spectrometry to be 0·3 [13] and 0·36 [14] at 12·5 and 10 V repeller fields, respectively. Tandem mass spectrometric experiments have shown that the rate ratio is dependent on ion translational energy, with the $H_2^-$ transfer reaction (2) becoming more important at lower energies.[24] We can evaluate the rate ratio in radiolytic systems from the relation

$$\frac{k_2}{k_2+k_8} = \frac{k_2}{k_1+k_2} \frac{G(C_2H_6)_{bimolec}}{G(CH_4)_{ionic}}$$

since $G(C_2H_4^+) = G(CH_4)_{ionic}$. All necessary values appear in tables 1 and 3 and the derived $k_2/(k_2+k_8)$ ratio is shown in table 4. Ratios were also derived from rare-gas-sensitized propane radiolysis data [10, 24] by a method consistent with the

direct radiolysis data. The value of $k_5/k_6 = 0{\cdot}51$ from our photolysis data was used in treating the rare gas mixtures in both gas and liquid.

TABLE 4.—INDIRECT CALCULATION OF $k_2/(k_2+k_8)$ FOR $C_2H_4^+$ IN IRRADIATED PROPANE

| scavenged system | $k_2/(k_2+k_8)$[a] | ref. |
|---|---|---|
| $C_3H_8$, gas, 25°C, 1 atm | 0·26 | 10 |
| $C_3H_8$+Kr, gas, 25°C, 1 atm | 0·37 | 10 |
| $C_3H_8$+Xe, gas, 25°C, 1 atm | 0·36 | 10 |
| $C_3H_8$, gas, 35°C, 1 atm | 0·49 | this work |
| $C_3H_8$, liq., 35°C | 0·64 | this work |
| $C_3H_8$, liq., −78°C | 0·51 | this work |
| $C_3H_8$, liq., −130°C | 0·43 | this work |
| $C_3H_8$+Ar, liq.,, −130°C | 0·40 | 25 |
| $C_3H_8$+Xe, liq., −78°C | 0·60 | 25 |

[a] reaction numbers refer to text; 2 = $H_2^+$ transfer; 8=$H^-$ transfer.

In table 4 our gas phase data do not agree with the more extensive data of Bone, Sieck and Futrell (BSF) [10]; this difference lies entirely in the observed $CH_4$ yields (table 3). If we take the more extensive data of BSF, $k_2/(k_2+k_8) = 0{\cdot}33\pm0{\cdot}05$, which is in excellent agreement with the mass spectrometric data.[13, 14] It is not clear that such agreement should be expected, however. The average of all liquid phase values gives $k_2/(k_2+k_8) = 0{\cdot}51\pm0{\cdot}09$. This is a *lower* limit since $G(CH_4)_{\text{ionic}}$ was calculated as an upper limit in the liquid. The BSF gas phase data indicate that $H_2^-$ transfer does become more important in the liquid while our gas phase data indicate that $H_2^-$ transfer may become more important in the liquid due to the lower limit restriction.

## EFFECTS OF PHASE CHANGE

Fig. 1 clearly shows that a change from gas at 1 atm to liquid at the same temperature decreases by 44 % the total number of propane molecules decomposing to give non-radical products. The analysis in table 3 allows us to discuss the effects of phase change on the two major precursors in the scavenged system, excited propane ions and excited neutral molecules.

On passing from gas to liquid radiolysis, the amount of ion decomposition decreases by 69 % as an upper limit while excited molecule decomposition decreases by only 7 % or less. The upper limit exists because we have not direct measure of ionic decomposition to give $C_3H_7^+$; it has been estimated to contribute 10 % of the total ion yield in the gas [10] and may perhaps be even more important in the liquid. Although parent ion fragmentation is greatly reduced in the liquid, the $C_2H_3^+$ yield demonstrates that some highly energetic fragmentation processes still occur. When the ion distribution derived for either gas or liquid is compared with calculated and experimental ionic breakdown curves,[11c] it is evident that the decomposing ions must have a broad distribution of energies from 1-4 eV in both gas and liquid.

The major *net* effect of the phase change is consistent with gas phase results in which increasing pressure decreases ionic fragmentation and leaves neutral molecule fragmentation relatively unchanged.[4] Although net excited molecule decomposition is little affected by phase, more parent ions are neutralized in the liquid to give excited molecules. Thus it cannot be concluded that individual excited molecule decomposition is unaffected by phase. In fact, table 3 shows that the net yield of molecular ethylene is decreased by 40 %. This feature is masked in the overall neutral molecule decomposition by the estimated increase in the molecular propylene yield.

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